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CATEGORIZATION (LISTING) BACKGROUND DOCUMENT

BENZENE

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Ontario

Environment
Environnement

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BENZENE

ONTARIO MINISTRY OF THE ENVIRONMENT

WASTE MANAGEMENT BRANCH

HAZARDOUS WASTE REVIEW UNIT

MAY 1990

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1.0 SUMMARY OF BASIS FOR CATEGORIZATION (LISTING)

1.1. Listing under Regulation 309

The Ontario Ministry of the Environment (M.O.E.) is considering amending Regulation 309 and listing Benzene in Schedule 1 as a hazardous industrial waste.

This could be achieved in two ways:

i) when benzene (or benzene mixture) is disposed of as a spent solvent or as still bottoms from the recovery of that same solvent, the waste would be listed as a non-specific source under Schedule 1, NA 9305;

ii) when residual benzene is found in waste generated during the manufacturing of the chemical (benzene) or from manufacturing of other chemicals from benzene, the waste streams would be listed in the source-specific section of Schedule 1. In this case benzene is used as a raw material, rather than as a solvent.

Benzene is already listed in Schedule 2B of Regulation 309, as a hazardous waste chemical. Hazardous waste chemicals include commercial chemical products or manufacturing intermediates that, from time to time, may be off-specification, or otherwise unacceptable for use.

Benzene exhibits the hazardous characteristic of ignitability and is a known carcinogen. If the waste

contaminated with benzene, is mismanaged either in handling, transportation or disposal, benzene would enter the environment. Because of its mobility and moderate persistence in groundwater, benzene would create a health hazard in drinking water.

1.2 Listing under other Canadian legislation.

Under the Ontario Occupational Health and Safety Act (administered by the Ministry of Labour), benzene is regulated as a designated substance. This regulation (O.R. 732-84) limits the exposure of workers to benzene by requiring emission control and personnel protection equipment.

Under the federal Transportation of Dangerous Goods Act (TDGA), benzene is listed as a dangerous good: flammable liquid (Class 3.2), or environmentally hazardous substance based on toxicity, bioaccumulation and persistence in the environment (Class 9.2). Benzene wastes may be classified as hazardous wastes, based on the same criteria defining dangerous goods. However, there is no further legislation regulating benzene wastes at the federal level.

Benzene is also listed in the proposed Federal Control Products Regulations (Canada Gazette, Part II, January 20, 1988, pp. 551) and therefore would be covered by worker right-to-know legislation in Ontario (WHMIS, O.Reg. 644/88 under the Ontario Occupational Health and Safety Act).

1.3 Listing under U.S. legislation

Benzene waste has been listed in the U.S. P.L. "Resource Conservation and Recovery Act" (RCRA) (CFR, 1987) as a hazardous waste if disposed of as a spent solvent or as still bottoms from the recovery operation of that solvent. Spent solvent has been defined in the U.S. legislation as follows:

a) the original chemical mixture must have a solvent property (i.e. dissolve or mobilize constituents);
b) the chemical mixture must be spent;
c) before use (i.e. at the commercial stage), the chemical mixture must have a total concentration of 10 per cent or more of the listed constituents.

In addition, benzene is also listed as a hazardous waste chemical when discarded as commercial chemical products, off-specification species, container residues and spill residues.

2.0 DESCRIPTION OF INDUSTRIAL SECTORS

The industrial sectors identified as potential generators of waste contaminated with benzene include the industrial sector producing the chemical, the sector using benzene as an intermediate to manufacture other chemicals, and any other industries using solvents or reagents containing benzene.

2.1 Benzene Production

Benzene is produced mostly from petroleum in refinery type operations. A minor portion of the benzene that is produced (about 15% in Ontario) comes from the light oil by-product of metallurgical coke production

Table 1 identifies the refineries producing benzene in Ontario and other provinces.

In petroleum refining operations, specific petroleum feed stocks (mostly reformates) are treated with solvent to extract the benzene portion. Benzene is then removed from the solvent/benzene mixture by steam distillation. Liquid waste generated from benzene refining is treated at the refinery wastewater treatment plant. Sludges from the treatment plant are already listed in Regulation 309, because of high levels of lead and chromium. Solid wastes from benzene refining include spent catalysts, column bottoms and residues.

The steel industries require large quantities of coke, which is produced by heating coal in ovens. The off-gases from the ovens are cooled to recuperate the by-products of the coke. After treatment of the by-products, the final product, called light-oil, contains nearly 70% benzene. In Ontario, light-oil is not processed further by the steel companies, but is shipped directly to refineries where the benzene is extracted by fractioning distillation (Holliday,1979b).

2.2 Use of benzene

Benzene, being the simplest of the aromatic compounds, is the chemical most used (after ethylene) in the production of industrial organic chemicals (see Table 2). Benzene is also used as a solvent and in a catalyst formulation in the production of styrene-butadiene rubber and latexes. Table 3 gives a summary of Canadian industries using benzene.

In Ontario, the majority of benzene is used in the production of styrene (nearly 70%, based on maximum capacity figures in Tables 1 and 3). Styrene monomer is made from ethylene and benzene, via the intermediate compound ethyl benzene, by a combination of alkylation and dehydrogenation. Waste contaminated with benzene and other organic chemicals are generated in the disposal of used catalysts from the ethylene/ benzene reactor and the dehydrogenation (of ethyl benzene) column. Contaminated residues are also generated from the recovery, dehydration and finishing columns.

Benzene is also used as a solvent in the manufacturing of styrene-butadiene rubbers. Butadiene is solution polymerized in benzene, in the presence of a catalyst. The rubber is then slurried with water, and benzene is removed and recycled. Benzene wastes are generated in the recovery and recycling processes as still bottoms and residues.

Although the use of benzene as solvent has been decreasing in Canada and the U.S.A. (IARC, 1982; Holliday et al., 1979b; Corpus, 1988) benzene can still be used in trade and industrial paint, rubbers, cements, adhesives, paint removers, artificial leather and rubber goods. Benzene has also been used in the shoe manufacturing industry, the rotogravure printing industry and chemical laboratories (OSHA, 1978; Mara et al., 1978; and USEPA, 1985).

Certain hydrocarbon solvents contain benzene in minor concentrations, varying from less than 0.1% to near 2%. Table 4 lists four broad types of solvents. The trend in the rubber processing industry has been to use solvents with minimal benzene content. In the adhesive and sealant industry, solvent based formulations are being replaced with hot-melt and

water-based adhesives. Similarly, paint and coating manufacturers are moving away from the use of solvent-based formulation (Holliday et al., 1979b).

3.0 WASTE MANAGEMENT PRACTICES

Waste Management practices vary from one type of generator to another. Consequently, the approach to reviewing waste management practices is to look separately at the practices of benzene manufacturers and users. Users include industries producing organic chemicals derived from benzene and industries using benzene as a constituent in solvents and reagents.

3.1 Benzene Producers

From the information available, it is difficult to evaluate how much benzene may be lost into the environment (through air emission, liquid effluent or solid waste disposal). Gilbert et al. (1982) has estimated the relative release of benzene in the three media as follows:

air:	80%
water:	16%
solid waste:	4%

Holliday et al. (1986) has derived an air emission factor in the benzene production industry as 2.5 kg/t of benzene produced. (Gilbert, in comparison, assumed a total emission factor averaging 1 kg/t).

Assuming that the relative benzene release factors are valid in Ontario industries, a release factor of 0.13 kg/t is derived for benzene in solid waste, i.e. (2.5 kg/t/0.80)x(0.04). From a total production of 299 kt of benzene in Ontario (1987 benzene production was 83% of maximum capacity, Table 1), this would represent 39 tonnes of benzene released in solid

waste per year in Ontario.

In the United States, the largest proportion (91%) of solid waste containing benzene and generated from petroleum refinery is disposed of in landfills and in lagoons (see Table 5). A small percentage (8.4%) is disposed of by land spreading or land farming. A negligible percentage (0.8%) is incinerated (Gilbert et al., 1982). The Land Disposal Restrictions of the Hazardous and Solid Waste Amendments (HSWA) of 1984 do not affect the waste management of waste contaminated with benzene from a refinery operation, since benzene is not considered a solvent or a waste chemical in this process (FR, 1986).

In Ontario, there are four companies producing benzene from refinery type operations (see Table 1). Under Regulation 309, these companies have registered most of their benzene wastes as hazardous industrial wastes, because these wastes are often mixed with listed wastes from the petroleum refining sector (Schedule 1). These registered hazardous industrial wastes are therefore managed according to Regulation 309 requirements, and disposed of as hazardous wastes.

3.2 Benzene users in chemical industries

As indicated in Table 2, benzene is predominantly used as a raw material for the synthesis of other organic chemicals. Six (6) chemical industries using benzene have been identified in Ontario (see Table 3). Although the release ratio of benzene in solid waste is not known, Holliday et al. (1986) derived an air emission factor of 12 kg/t of benzene used in ethyl benzene/styrene production and other processes using benzene as medium. As indicated by the same author this represents a high estimate for ethylbenzene

styrene production. Gilbert et al. (1982) estimated an air emission of 2.7 kg/t for this process. Based on a production of 327 kt for 1987 in Ontario (i.e. 83% of maximum capacity of 394 kt, in Tables 1 and 3), this would represent 883 t/year of air emissions from chemical production, derived from benzene. To derive a benzene release into solid waste, we have to assume that the relative emission between media is in the same range as for benzene production (i.e. 80% in air and 4% in solid waste). This ratio would indicate that about 44 tonnes of benzene could be released in solid waste in Ontario from industries producing chemicals from benzene (i.e. (883 t / 0.80) x 0.04).

The waste management practice of benzene contaminated wastes from the chemical producers, identified in Table 3, has been reviewed from records of the Generator Registration Reports. The hazardous wastes, or waste contaminated with benzene, are either used as waste derived fuel (or incinerated) at licenced plant facilities, disposed of at on site landfills (licenced to accept hazardous wastes) or sent to Tricil hazardous waste landfill. There is no indication that process wastes are disposed at municipal landfills.

3.3 Benzene used as solvent-reagent

Although the total demand for benzene in Canada and Ontario has steadily increased over the last decade, the use of benzene in solvents and reagents has decreased (Holliday et al., 1979b; Corpus, 1988) due to new legislation restricting its use in the working environment (designated substance in 1987, by the Ontario Ministry of Labour). The increasing demand has been in most part from the ethylbenzene production industry.

Similarly in the U.S., benzene used as solvents has decreased, since the 1977 ban on the use of benzene in consumer goods by the consumer Products Safety Commission (Neufeld et al., 1978).

The majority of the benzene used as solvent is either released to the air or discharged as effluent. The percentage of air emission can range from 50% to 100% of benzene released in the environment, depending on the type of use. Releases of benzene due to disposal of solid residues are considered small and difficult to quantify (Neufeld et al., 1978). To make a reliable evaluation of benzene release from solid wastes disposal, one would need:

- the production of benzene-containing residue;
- the percentage of benzene (by weight) of the residue;
- the method of waste disposal.

In 1987, about 1000 tonnes of benzene were used for miscellaneous applications in Canada (see Table 2). Assuming that 35% (relative population of Ontario) of this amount was used in Ontario, and assuming a fraction of this amount is used as solvent, the best estimate for the amount of benzene released in solid waste would be in the range of a fraction of a tonne in Ontario.

Waste contaminated with benzene solvent is either disposed of as a registered hazardous waste (if the quantity of benzene or other listed solvents are appreciable by the generator) or disposed of in the effluents or as a non-registered solid waste. The quantity is however considered small and difficult to quantify.

4.0 HAZARDOUS PROPERTIES OF WASTE

The behaviour of any pollutant depends on its chemical and physical properties. By and large, the chemical properties govern the eventual fate of the compound while physical properties govern its transport and distribution through the environment.

4.1 Environmental Fate

Benzene is not reactive as defined in Regulation 309. The main reaction in the environment involves the chemical degradation of benzene with the hydroxyl radical OH in the lower atmosphere (troposphere). Biological degradation, involving specific enzymes, is an important fate process for both the soil and water system.

4.2 Physical Properties

The main physical properties of benzene relevant to its environmental transport and distribution are presented in Table 7. The volatility of benzene (vapour pressure of 10.0 kPa) and its water solubility (1,780 mg/L) are the driving force behind the behaviour of benzene in the environment. This behaviour is reflected in the partition coefficient which governs the distribution of benzene between the various environmental sectors: for example, benzene being water soluble and volatile, significant concentrations of the solvent can be carried by ground and surface water, as well as in the air.

4.3 Hazardous Characteristic

Pure benzene, with a flash point of -11.1°C, is considered ignitable under section 1(29) of Regulation 309. It is expected that, when pure benzene is used as a solvent, the corresponding spent solvent will also exhibit the characteristics of ignitability.

Benzene is not considered reactive, corrosive or leachate toxic under Regulation 309.

4.4 Environmental Behaviour

The exposure pathway of principal concern in waste management is disposal in a landfill and subsequent contamination of groundwater.

4.4.1 Mobility

The water solubility of a given hazardous constituent is indicative of its mobility potential (i.e. likelihood that it will be released from a management site and become dissolved in a water resource of concern). The relatively high solubility of benzene in water is an indication of its high mobility: the concentration of 1780 mg/L (solubility of benzene in water) is several orders of magnitude of the safe concentration of 0.02 mg/L (Ontario Water Quality Guideline). The log octanol/water partition coefficient of 2.12 is another indicator of the high mobility of benzene. According to Briggs (1973) this K_{OW} value means that benzene has a moderate to high affinity for water, and is not expected to be immobilized to a significant degree by sorption to soil with a high organic content.

4.4.2 Persistence

Benzene does not react with water in the pH range of 2 through 14. Although benzene will readily burn if ignited (flash point = -11°C) it does not spontaneously react with oxygen at ordinary temperature and pressure. Since it does not absorb visible light, it will not be directly photolyzed in the lower atmosphere or surface water (USEPA, 1985b).

Benzene is subject to biodegradation in aerobic soil and water (Gibson, 1968). Bacteria convert benzene to catechol

using a dioxygenase enzyme. However the rate of degradation appears to be slow (Gibson et al., 1984). Also there is evidence of anaerobic degradation but the mode in which it occurs is not clear (USEPA, 1985b).

Although benzene is expected to degrade through hydroxyl radical oxidation in the atmosphere (half-life less than 10 days) and biodegradation in surface waters (half-life less or near 10 days, Holliday et al., 1986) it is expected to be slightly persistent in ground water due to its relatively high solubility in water and the relatively low level of biological activity in ground water (USEPA, 1985b).

4.4.3 Bioaccumulation

The bioconcentration factor (BCF) has been estimated to be 24 for aquatic organisms that contain 8% lipids. (US EPA, 1980). A BCF value of 890 was reported for Green Sunfish (ISHOW database). Based on the correlation between BCF and K_{ow} developed by Veith et al. (1980) (i.e. log BCF = 0.76 (log K_{ow}) - 0.23) the estimated BCF value is 23.5.

4.4.4 Environmental Exposure

In waste management, the exposure pathway of principal concern is leaching of benzene to ground water. The water solubility (1780 mg/L) being near 5 orders of magnitude greater than the corresponding Provincial Water Quality Guideline (PWQG) of 0.02 mg/L, the potential of environmental exposure is high. A U.S. study indicates that benzene concentration in leachate around 0.1 mg/L (ppm) have been measured in residential wells adjacent to landfill sites (Stuart et al, 1985; see Table 8)

Another concern is the air emission of benzene from benzene contaminated wastes in landfills. Because the compound is highly volatile (10.0 kPa at 20° C), waste contaminated with high concentration of benzene could be an important source of air emission.

4.5 Toxicity

4.5.1 Plants

In the alga Chlorella sp., benzene has been found to be toxic, causing inhibition of cell growth and photosynthesis, and ultrastructural alternations in chloroplasts and pyrenoids (Wardas, 1984). Growth inhibition was also noted in other studies on freshwater and marine algae (EPS, 1984).

4.5.2 Invertebrates

Given the importance of earthworms (Eisenia foetida) to soil quality, it is noteworthy that benzene is acutely toxic when administered by contact to these invertebrates (Newhauser et al., 1985).

In insects, benzene has an LD_{50} of 210 mg/L for grain weevils and an LD_{50} of 59 mg/L for mosquito larvae (NRC, 1981).

4.5.3 Vertebrates

For freshwater fish, lethal doses of benzene (assessed by LC_{50}, LD_{50}, TLm) range from 6 to 425 mg/L, over a range of experimental conditions. For other marine fish, the range is similar at 4 to 386 mg/L (Neff, 1979; EPS, 1984).

4.5.4 Animals

Chronic exposure of rats and mice to benzene administered orally and of rats to benzene by inhalation has resulted in multi-site induction of cancer (Maltoni et al., 1982: NTP, 1986).

Benzene has a low acute toxicity to animals. Inhalation of air concentrations of about 10,000 ppm and above for several hours has been shown to be fatal to a range of species, death being due to the direct narcotic effect of benzene. The threshold for narcotic effects has been estimated to be about 4,000 ppm (Fielder et al., 1982). Oral toxicity studies (i.e. by ingestion) indicate LD_{50} of around 4-5 g/kg in adult rodents (Fielder et al., 1982).

Several inhalation studies have been carried out to investigate the teratogenicity of benzene. Exposures between 800 and 2,700 ppm have produced fetotoxic effects (reduced fetal weight and skeletal effects indicative of delayed development) (Fielder et al. 1982). The dose-dependent fetotoxic effects of benzene have been confirmed by Ungvany and Tatrai (1985) in laboratory rodents.

4.5.5 Humans

Long-term inhalation, in humans, of high concentrations of benzene (e.g. industrial exposure levels of tens or even hundreds of ppm) has resulted in a variety of haematopoietic and blood cell abnormalities, as well as damage to the central nervous system (Fielder et al., 1982).

Chronic exposures of benzene which produced marked effects on blood may eventually result in leukemia (Rinsky et al., 1981, 1987)

Benzene is not known to cause any teratogenic effects in humans (Barlow et al., 1982).

According to IARC (1982), the examination of bone marrow precursor cells and some white blood cells (lymphocytes) of humans exposed to benzene has shown changes in the generic material (chromosomes) of the cell. At sufficiently high levels, there is complete destruction of bone marrow precursor cells and a resultant decrease in red blood cell count, white blood cell count and platelet count (Goldstein, 1988).

Benzene has been classified as a known human carcinogen (Group A) according to the EPA Guidelines for Cancer Risk Assessment (USEPA, 1985b; 1986). Benzene is also considered to be a carcinogen by the Occupational Safety and Health Administration (OSHA, 1978; 1987), the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC, 1987).

In Ontario, benzene is classified as a "designated substance" by the Ministry of Labour. The Ministry of the Environment has included Benzene in the Ontario Effluent Monitoring Priority Pollutant List, due to its demonstrated carcinogenicity (MOE, 1987). The Provincial Water Quality Guideline (PWQG) has been set at 0.02 mg/L for benzene (Bazinet, 1989). This level protects any taste or odour effect in water, as well as protecting all forms of aquatic life. Guidelines are developed when sufficient data on aquatic toxicity do not exist for the development of objectives. Guidelines are over-protective and more stringent than objectives, because of paucity in the toxicity data.

The minimum acceptable concentration for drinking water is set at 0.005 mg/L by Health and Welfare Canada.

4.6 Results of the Vector Scoring System

A Vector Scoring System for Waste Categorization and Review has been developed to evaluate the toxicity and exposure of waste to human health and the environment. The results of the Vector Scoring System for benzene are shown in Table 9. Details of the scoring procedure are presented in the Guidance Manual (MOE, 1988). The human toxicity and the carcinogenic properties of benzene are the paramount concerns in the health effect assessment. There is epidemiological evidence that benzene causes leukemia in humans. The environmental parameters of concern are the high mobility and slight persistence of benzene. Leaching to groundwater from a landfill site and contamination of drinking water is also a significant health hazard.

The justifications of the scoring are presented in Appendix C.

5.0 Conclusions and recommendations

Solid waste contaminated with benzene are generated from three types of operations:

- ° benzene production (petroleum refineries mostly);
- ° organic chemical manufacturing, using benzene;
- ° users of benzene mixture as solvent/reagent.

Benzene wastes generated in the production process (refinery) are part of the influent of refinery wastewater treatment plant. Sludges from petroleum refineries are already listed in Schedule 1 and are therefore managed as hazardous wastes.

Benzene waste generated from organic chemical manufacturing are in the form of spent catalysts contaminated with

benzene, reactor and column bottoms and residues. These streams are not listed in Regulation 309 at this time.

Although the use of benzene or benzene mixture as solvent has been decreasing over the last decade, spent benzene can still be a hazard to health and the environment.
At present, spent benzene used as solvent is not listed in Schedule 1.

Benzene loss to the environment is primarily through air emission (nearly 80%) and effluents (nearly 16%). Solid wastes disposal represent about 4% of the total benzene loss. There may be provincial or regional variations around these figures, due to the types of industry and emission control regulations.

Benzene is a known carcinogen. High benzene mixtures are also ignitable. Although benzene is highly volatile, the chemical is also considered mobile in ground water. Due to these characteristics, benzene can create a health hazard.

Due to its toxicity (i.e. carcinogenicity and toxic effects on blood-forming systems and nervous systems) and its exposure potential, (i.e. mobility) it is recommended that benzene contaminated wastes be listed in Regulation 309. Specific waste streams have been identified in the organic chemical manufacturing industry where benzene wastes are produced. It is recommended that these specific streams be listed in Schedule 1 of Regulation 309 (see Appendix D). Because of the varied use of benzene or benzene mixture as solvents, it is difficult to list these wastes as specific waste streams. Therefore it is recommended that any benzene or benzene mixture, in the form of spent solvents or still bottoms from the recovery of these solvents be listed under "non-specific sources" in Schedule 1. (See Appendix D).

TABLE 1

CANADIAN INDUSTRIES PRODUCING BENZENE

	Company	Plant Location	Maximum Capacity (kt/year) (1987)	
Ontario				
	Sunchem	Sarnia	55	
	Shell Canada	Corunna	65	
	Esso Chemical Canada	Sarnia	100	
	Petrosar	Corunna	140	
		Sub-total		360
Quebec				
	Kemtec Petrochemical Corp.	Montreal[1]	117	
	Petrocan Chemicals	Montreal	155	
		Sub-total		272
Alberta				
	Shell Canada	Scotford	235	
		Sub-total		235
		Total		867[2]

1. Previously run by Gulf Canada
2. The actual domestic production for 1987 was 719.6 kt (83% of the maximum capacity). With 24.9 kt as imports, a total of 744.5 kt was used in Canada.

Source: Corpus, 1988. CPI Product Profiles, Benzene. Corpus Information Services, June 1988.

TABLE 2

BENZENE USE IN CANADA (1987)

Chemical Produced	Benzene Use (kt/yr)	%
Ethylbenzene/styrene	524	70.4
Cumene	40.3	5.4
Cyclohexane[1]	0	0
Maleic anhydride	10	1.3
Miscellaneous	1	0.1
Sub-total	575.3	77.3
Export Sales	169.2	22.7
Total Use:	744.5	100.0

Source: Corpus, 1988.
CPI Product Profile; Benzene. Corpus Information Services, June 1988.

1. The cyclohexane facilities of Gulf Canada (Montreal East refinery) were closed down in December, 1985. The only user of cyclohexane, Du Pont Canada (Maitland, Ontario), is being supplied by a U.S. source.

TABLE 3

CHEMICALS PRODUCED FROM BENZENE (1987)

Chemical	Company	Location	Max. Capacity (k tonnes/year)
Styrene	Dow Chemical Can.	Sarnia, Ont.	70
	Polysar	Sarnia, Ont.	272
	Shell Can. Chemical	Scotford, Alta.	308
		Total	650
Styrene-Butadiene			
Rubber	Polysar[2]	Sarnia, Ont.	0
Latexes	BASF	Sarnia, Ont.	26.5
	Dow Chemical Can.	Sarnia, Ont.	14.0
	Dow Chemical Can.	Varennes, Que.	14.0
		Total	54.5
Cumene	Gulf Canada	Montreal, Que.	0[1]
Maleic Anhydride	BASF Canada	Cornwall, Ont.	2
	Bartek Chemical	Burlington, Ont.	9
	Monsanto Canada	Montreal, Que.	7
		Total	18

Source: Corpus, 1988.
CPI Product Profile; Styrene, Cumene, Maleic Anhydride. Corpus Information Services, June, 1988

1. The refinery was shut down in December, 1985

2. Unit shifted to nitrile butadiene rubber in July, 1986.

TABLE 4

TYPES OF HYDROCARBON SOLVENTS CONTAINING BENZENE*

CLASSES	TRADE NAMES (Examples)	BENZENE CONTENT (Typical)	USES
Light naphtha (low, narrow boiling range)	Iosol 1520 Gulfsol 1420 Benzo Sol 12	2 to 2.3%	Contact cements Lacquers Printing inks
Heavier naphtha (higher boiling range)	Iosol 2024 Gulfsol 2024 Tolu Sol 20	0.1 to 0.2%	Adhesives Coatings Inks
Rubber processing solvents (low boiling, low benzene)	Iosol 1426 Gulfsol 1426 Benzo Sol 2	0.2%	Rubber processing Adhesives Coatings
Pure Chemicals:			
Hexane		0.1 to 0.4%	Vegetable oil extraction Quick drying adhesives Rubber processing
Toluene, Xylene		0.1%	As benzene
		Typically 0.03 to 0.07%	substitutes Quick drying lacquers Paint strippers

* Source: Holliday et al., 1979b.

TABLE 5

WASTE MANAGEMENT PRACTICES FOR BENZENE WASTES

IN U.S. PETROLEUM INDUSTRY[1]

Disposal Method	Estimated Benzene Disposal (t)	Percentage of total Benzene
Landfilling	116	51.1
Landspreading	19	8.4
Lagooning	91	39.7
Incineration	2	0.8
Total	228	100.0

1. Source: Gilbert et al. 1982

TABLE 6

U.S. USE OF BENZENE (1978)*

Product	Production (10^6 kg)	Benzene Required (10^6 kg)	Ratio Benzene/Product	% Benzene Use
Ethylbenze	3,803	2,810	100:135	53.6
Cumene	1,533	1,030	100:149	19.6
Cyclohexane	1,057	836	100:126	15.9
Nitrobenzene	261	170	100:154	3.2
Chlorobenzene	172	134	100:128	2.6
Alkylbenzene	330	132	100:250	2.5
Maleic anhydride	155	132	100:117	2.5
Biphenyl	29	7	100:414	0.1
Total	7,340	5,251		100

* Source: Gilbert et al., 1982

TABLE 7

Selected Physical Properties of Benzene*

PROPERTY	VALUE	COMMENTS AND REFERENCES
Molecular formula	C_6H_6	
Molecular weight	78	
PROPERTIES OF PURE BENZENE		
Melting point	5.5°C	[Weast, 1971]
Boiling point	80.1°C	[Weast, 1971]
Density	0.87 g/cm^3	[Holliday et al., 1979a]
Saturated vapour pressure	12.7 kPa @ 25°C 10.0 kPa @ 20°C 7.8 kPa @ 15°C 6.1 kPa @ 10°C	Interpolated from vapour-pressure data presented by Stull [1947], using the Clausius-Claperyon equation.
Water solubility	1.78 g/L @ 25°C 1.75 g/L @ 10°C	[MacKay and Lionen, 1975]
Solubility in common organic solvents	Completely miscible	[Weast, 1971]
PARTITION COEFFICIENTS		
Air/water (Henry's Law constant, H)	5.5×10^{-3} atm.m^3/mole @ 25°C 2.7×10^{-3} atm.m^3/mole @ 10°C	Calculated assuming that benzene behaves ideally: H = saturated vapour pressure/water solubility (units of atm and mole/m^3, respectively)
Soil/water, K_{OC} (based on organic carbon content)	83	Average of experimentally measured partition coefficients using naturally occurring sediment samples [Karrickhoff et al., 1979]
	92, 100	Experimental values obtained from two soils (2.6% and 1.8% organic content, respectively) [Rogers et al., 1980]
Octanol/water, K_{OW}	130	Experimentally measured [Karrickhoff et al., 1979]
CONVERSION FACTORS		
Benzene in air	1 ppb = 3.2 µg/m^3 @ 25°C = 41 nmole/m^3 @ 25°C 1 ppb = 3.4 µg/m^3 @ 10°C = 43 nmole/m^3 @ 10°C	Calculated assuming that benzene behaves as an ideal gas. N.B. In this case "ppb" are partial pressures (in atmospheres) and are essentially molar quantities.
Benzene in water	1 ppb = 1 µg/L = 13 nmole/L	N.B. In these cases, "ppb" are gravimetric quantities.
Benzene in soil/biota	1 ppb = 1 µg/kg = 13 nmole/kg	

* Source: Holliday and Engelhardt, 1986.

TABLE 8

Benzene Levels in Water Samples (1)

Source type	Location	Concentration (ppb)	Comments	References
Drinking water	United States	NQ	24 documented occurrences	Shackelford and Keith, 1976
		0.1 to 0.3		USEPA 1980
		<0.2 (avg.)	7 of 113 sites positive	Brass et al., 1977
		50	Presumably an average of 700 samples (1975)	Kraybill, 1977
	Ontario	0.4	Absorption/desorption of benzene from anthracite coal screenings used as filter medium	Smillie et al., 1978
Ground water	New York, New Jersey, Connecticut	30-330	Contaminated well water	Burmaster, 1982, as reported in CHEMFATE 1987
	United States	>100	Well water from Jacksonville, Florida	USEPA 1980
		NQ	8.5% occurrence in a federal survey	Dyksen and Hess, 1982
Ground water	United States	NQ to 100	Found in leachate from some residential well adjacent to a landfill; deep drinking well had highest concentration	Stuart et al., 1985
Surface water	Ontario	<.1	Raw water of water treatment plants	Ontario Drinking Water Surveillance Program(2)
Ground water	Ontario	<.05	Well water	Ontario Drinking Water Surveillance Program(2)

NQ = not quantified

(1) Source: Oak Ridge National Laboratory, 1987

(2) Data from Ontario Drinking Water Surveillance Program, Water Resources Branch, MOE, 1988.

TABLE 9

RESULTS OF VECTOR SCORING FOR BENZENE

	Parameter	Score (0-10)	Concern Levels+
1.	Environmental Transport	7	≥ 7
2.	Environmental Persistence	2	≥ 7
3.	Bioaccumulation	4	≥ 7
4.	Environmental Exposure	7	≥ 7
5.	Acute Toxicity	4	≥ 6
6.	Sublethal effects, plants	2	≥ 4
7.	Sublethal effects, mammals	4	≥ 4
8.	Sublethal effects, non-mammals	*	≥ 4
9.	Teratogenicity	0	≥ 2
10.	Mutagenicity	10	≥ 6
11.	Carcinogenicity	10	≥ 2

+ : Concern levels established for the listing of hazardous wastes.

* : Insufficient data.

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APPENDICES

Appendix A: US REGULATIONS

The US EPA has defined spent solvents as those solvents that are used for their "solvent" properties that is to solubilize (dissolve) or mobilize other constituents (for example, solvents used in degreasing, cleaning, fabric scouring, as diluents, extractants, reaction and synthesis media). A solvent is considered "spent" when it has been used and is no longer fit for use without being regenerated, reclaimed or otherwise reprocessed.*

The listing of spent solvents was originally drafted with the intention to include technical grade, practical grade or pure forms of the solvents. On December 31, 1985 the listed solvents

were to include mixtures containing ten percent or more total listed solvent. The ten percent threshold applied to solvent mixtures, before use. The agency took this position based on data which indicate that solvent mixtures used in commerce, typically contain more than ten percent total solvents.*

* U.S. Federal Register, Final Rule, Vol 51, Feb.25, 1986, p.6537-6542.

Appendix B: SOURCES AND ENVIRONMENTAL EMISSIONS

B-1: Benzene in the Canadian Industry

In 1979, Arthur Sheffield published a Canadian inventory of sources and emissions of benzene (see Table 1 for the 1976 summary.) Benzene emissions occur during crude oil operations, (i.e. production, transportation and storage), petroleum refinery operations (production of benzene and gasoline), coke oven operation (production of coke from coal) and from mobile source (exhaust and evaporation from powered motor vehicles).

The major source of benzene air emission identified in the inventory are:

1. the exhaust of powered vehicles (77.0 to 83%)

2. the use of benzene as a starting material in the production of derivatives (e.g. production of styrene) (6.6 to 7.2%)

3. the use of benzene in surface coating applications (3.8 to 4.2%)

Since the 1976 inventory the use of benzene in the paint industry (surface coating) has been significantly reduced.

TABLE B-1 Summary of Benzene Emissions, Canada 1976

Source	Air Emissions (tonnes)	% of Total (*)	% of Total (**)
Crude Oil Operations	92	0.21	0.20
Petroleum Refineries			
a) General			
1. Refinery operations	175	0.40	0.37
2. Gasoline storage	62-488	0.14	1.04
b) Benzene Production			
1. Process	125	0.29	0.27
2. Storage	803	1.85	1.71
Chemical Processes Using Benzene and its Derivatives	3,103	7.15	6.62
Coke Ovens	124	0.29	0.27
Mobile Sources			
a) Gasoline-Powered Motor Vehicles			
1. Exhaust	36,079	83.22	77.00
2. Evaporative	297-2,350	0.69	5.02
b) Diesel-Powered Engines			
1. Trucks	100	0.23	0.21
2. Railway	180	0.42	0.38
3. Marine	137	0.32	0.29
Fuel Combustion in Stationary Sources	unknown		
Miscellaneous			
a) Benzene Loading/Unloading Operations	102	0.24	0.22
b) Gasoline Marketing			
1. Distribution	23-179	0.05	0.38
2. Service stations	125-991	0.29	2.12
Surface Coating Applications	1,790	4.12	3.82
Asphalt Plants	38	0.09	0.08
Miscellaneous Chemical Industries	unknown		
Total	43,355-46,856	100.00	100.00

* Based on maximum total Canadian emissions.
** Based on minimum total Canadian emissions.

Source: Sheffield, 1979. National Inventory of Sources and Emissions of Benzene (1976), Pollution Data Analysis Division, Air Pollution Programs Branch Air Pollution Control Directive, Report EPS3-AP-79-41 September 1979.

B-2: Benzene in the Ontario Industry

Holliday et al (1986)* conducted a similar survey in Ontario for 1984. Table 2 summarizes the Ontario air emissions. The major sources of benzene emission in Ontario were:

1. the exhaust of gasoline-powered vehicles (70.6%)

2. the use of benzene as a chemical derivative (24.1%)

3. benzene production 4.2%

The lower gasoline emission percentage in Ontario compared to the total Canadian sector results from the fact that the major petrochemical and coking activities are in Ontario.

* Holliday, M.G. et al. 1986. Benzene:

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TABLE B-2 Major Sources and Air Emissions of Benzene (Ontario 1984)

Source	*Benzene Emission Factor	**Quantity Multiplier for Ontario	Ontario Emissions	Comments	Canadian Emissions (for Comparison)
PETROLEUM REFINING					
Crude Oil Operations	0.17 g/m^3 of crude oil stored at Ontario refineries	$29 \times 10^6 m^3$	5 t	This amount arises from storage of crude oil at refineries; amount from well-head operation in Ontario is negligible	78 t
Refinery Operations	1.8 g/m^3 of crude oil charged	$29 \times 10^6 m^3$	52 t	Does not include refinery activities resulting in benzene production	150 t
Gasoline Storage	10 g/m^3 of gasoline consumed	$12 \times 10^6 m^3$	120 t	Based on an average benzene content of 2% in gasoline	320 t
PETROCHEMICAL ACTIVITIES					
Benzene Production	2.5 kg/t of benzene produced	280,000 t	720 t	Assuming that benzene production in 1984 in Canadian facilities was in proportion to their nameplate capacities. Emissions comprise production (14%) and storage (86%)	1,400 t
Benzene Loading/ Unloading	0.1% of total benzene shipped other than by pipeline	73,000 t benzene shipped	73 t	Most benzene transported in Ontario is by pipeline (or is captive production) to the 2 producers of ethylbenzene /styrene	160 t
Benzene Use	12 kg/t of benzene used	340,000 t	4,100 t	This is an aggregated figure and comprises emissions from ethylbenzene/styrene manufacture and from processes in which benzene is used as a process medium	5,200 t
COKING OPERATIONS	16g/t of coal charged	6.0×10^6 t	96 t	Assuming that the steel companies of Ontario use 90% of coking coal imported into Canada	110 t
GASOLINE HANDLING					
Distribution	3.7 g/m^3 of gasoline sold	$12 \times 10^6 m^3$	44 t	Assuming an average benzene content 2% in gasoline	120 t
Service Stations	20 g/m^3	$12 \times 10^6 m^3$	240 t	2% benzene in gasoline; includes filling storage tanks, refuelling displacement losses, spillage	660 t
MOBILE SOURCES					
Gasoline Powered Vehicles	1.0 kg/m^3 of gasoline sold	$12 \times 10^6 m^3$	12,000 t	Assuming 2% benzene in gasoline; about 7% of the emissions come from evaporation losses, the remainder is from exhaust gases	33,000 t
Diesel Powered Vehicles	23 g/m^3 of diesel fuel sold	$3.8 \times 10^6 m^3$	90 t	The amount of benzene in diesel fuel is negligible; these emissions are all from exhaust gases	300 t
TOTALS			17,000 tonnes		41,000 tonnes

NOTE: The quantities in this table are with the exception of the quantity multipliers (which can be obtained to the nearest single unit from Statistics Canada tabulations), gross approximations for this reason, the data are expressed only to two significant figures.

* Derived, in the main, from information presented by Sheffield [1979] and appropriate Statistics Canada tabulations (details of derivations presented in the Appendix).

** Obtained, except where noted, from Statistics Canada production and use data for 1984

SOURCE: Holliday, et al 1986.

Appendix C: Justification of Vector Scores

	Element	Score	Justification
(1)	Environmental Transport	7	Fugacity Model (Level I) identifies two media >5%: air (94.6%) and water (5.3%).
(2)	Environmental Persistence	2	Majority of half-life measurements are less than or near 10 days.
(3)	Bioaccumulation	4	Log K_{ow} = 2.11
(4)	Environmental exposure	7	Because of easy pathway between the contaminant source and the receptor.
(5)	Acute Toxicity	4	Aquatic toxicity 96 hr LC_{50} = 31 mg/l.
(6)	Sublethal effects, plants	2	Several aquatic plants are unaffected by benzene concentration up to 10 mg/l.
(7)	Sublethal effects, mammals	4	No myelotoxic effects were observed in rats, guinea pigs or dogs at inhalation exposures levels of 56 mg/m^3 (17.6 ppm) benzene over 127 days.
(8)	Sublethal effects, non-mammals	*	Insufficient evidence.

	Element	Score	Justification
(9)	Teratogenicity	0	Not believed to produce teratogenic effects
(10)	Mutagenicity	10	Positive mutation *in vivo* of Drosophila Melanogaster
(11)	Carcinogenicity	10	Considered a carcinogenic (IARC)

* Insufficient data.

Appendix D: Proposed Amendments to Regulation 309

1. Schedule 1, NA9305

   "The following spent non-halogenated solvents: toluene, methylethylketone, carbon disulphide, isobutanol, pyridine, and benzene; and the still bottoms from the recovery of these solvents".

2. Schedule 1, following NA9341

   "Spent catalyst, column bottoms and residues in the production of styrene from benzene".

DO/ss

D7; OKUHARA, 0116R